INVESTIGATION OF SYNTHETIC FLUIDS BASED ON N-SUBSTITUTED MELAMINES

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Translation of: " Uber die Untersuchung synthetischer Flussigkeiten auf der Basis N-substituierter Melamine," In: Ardöl und Kohle, vol. 25, no. 6, June 1972, pp. 317-322.

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Investigation of N-substituted melamine based synthetic fluids

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Dedicated to Professor (Dr. Ing.) Friedrich Asinger on his 65th birthday.

Abstract: Derivatives of resonance stabilized heterocyclic compounds, such as for example s-triazines, seem to be suitable lubricant bases, due to their structure, showing high thermal and oxidation stability. Starting from 2,4,6-trichloro-s-triazine and secondary amines, symmetric and asymmetric substituted 2,4,6-(di-alkylamino)-s-triazine derivatives were synthesized and their thermal stability and thermal oxidation stability was investigated. Furthermore, their viscosity, viscosity-temperature dependence, and low temperature properties were determined. The obtained results were compared with those of known esters and polyphenyl ether based synthetic oils.

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Introduction

Since the requirements of practice in several cases exceeded the performance of mineral oil based lubricants, the problems of lubricating technology of the modern practice resulted in growing use of synthetic products.

Based on the fundamental work of Murphy and Zismann [1] and Zorn [2], synthetic lubricants were developed and used initially on the basis of di-esters of aliphatic dicarbonic acids (for example sebacic acid-di-(2-ethyl hexyl)-ester) and of sterically hindered esters on the basis of two-, three-, and four-hydric alcohols (for example trimethylol propane,

*Numbers in the margin indicate pagination in the foreign text.

pentaerythrit) esterified with C_7-, C_8-, or C_9-acids. The thermal and oxidation stability of these lubricants could be increased by the use of additives. For even higher requirements of thermal and oxidation stability, which could not be met with the ester-oils, mainly polyphenyl ethers were tested for their high temperature stability as lubricants and were used in special cases. Investigations were made on further groups of compounds, such as polyphenyl amines and perfluorinated organic compounds [3].

Several studies [4,5] indicated the usefulness of resonance stabilized heterocyclic compounds, such as 1,3,5-triazine, or cyclic trimers of phosphornitrile chloride as basic materials for the development of synthetic lubricants.

The 1,3,5-triazine seems to be of special interest in this relation. On one hand, this ring system based on its aromatic, resonance stabilized character [4] shows good thermal and oxidation stability [6]; on the other hand the 2,4,6-trichlorotriazine is easily prepared by trimerization of cyanogen chloride and represents a product, which can be used due to its reactivity, which can be compared with that of acyl halogenides, to prepare a multitude of derivatives with C-substitution in the ring system. The present work reports on selected alkyl-melamines and on the first studies of their potential application as a basis of synthetic oils. /318

Synthesis products and their physical properties

Starting with 2,4,6-trichloro-s-triazine and sec-n-alkyl or iso-alkyl amines, respectively, a series of alkyl melamines was prepared corresponding to the general formula (I) of Fig. 1.

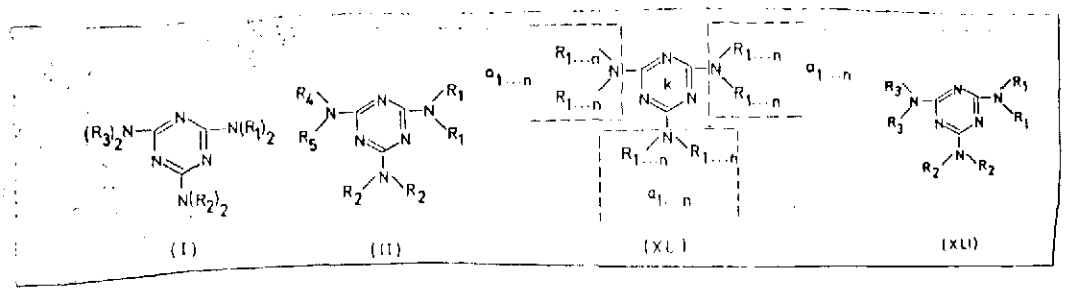

Figure 1. Formulas I, II, XL, and XLI (Explanation in the text)

Besides symmetrical derivatives ($R_1 = R_2 = R_3$), asymmetrical 2,4,6-tri-(di-alkylamino)-s-triazines ($R_1 = R_2 \neq R_3$ or $R_1 \neq R_2 \neq R_3$) were prepared by stepwise substitution of the 3 chlorine atoms of the 2,4,6-trichloro-s-triazine.

Further structural variations were achieved using non-symmetrical secondary amines as starting materials in the synthesis. The obtained compounds correspond to the general formula (II) in Fig. 1.

The following types of compounds were prepared:

a.) $R_1 = R_2$ - n-alkyl- or iso-alkyl-group
R_4 - n-alkyl group
R_5 - aryl- or alkylated aryl- or cycloalkyl- or benzyl-group

b.) $R_1 \neq R_2$ - n-alkyl group
R_4 - n alkyl-group
R_5 - aryl-group

The side chains were systematically varied, to determine and investigate the relationships between selected physical properties of the alkyl melamines and their chemical composition and to develop basic correlations if possible.

Table 1 summarizes the prepared compounds and several physical properties, such as boiling point, pour point, viscosity,

and viscosity-temperature relationship. These properties should be of interest in their application as a basis for oils.

Table 1

Basic data of the synthetic products

Number	Synthetic product	Boiling point °C 3 mm Hg	Pour point °C	Viscosity cSt 100°F	Viscosity cSt 210°F	V.I.
	1. Group					
III	2,4,6-Tri-(di-methylamino)-1,3,5-triazine		(Fp. 165°C)			
IV	2,4,6-Tri-(di-ethylamino)-1,3,5-triazine	145…147	(Fp. 12°C)	61,4	5,4	—81
V	2,4,6-Tri-(di-n-propylamino)-1,3,5-triazine	—	(Fp. 68°C)	—	10,3	—
VI	2,4,6-Tri-(di-n-butylamino)-1,3,5-triazine	210…212	(Fp. -4°C)	127,9	12,6	98
VII	2,4,6-Tri-(di-pentylamino)-1,3,5-triazine*)	230…231	— 26	535,8	25,1	62
VIII	2,4,6-Tri-(di-n-hexylamino)-1,3,5-triazine	280…285	(Fp. 12°C)	114,0	13,4	118
IX	2,4,6-Tri-(di-n-octylamino)-1,3,5-triazine	324…327	(Fp. 32°C)	—	13,8	—
X	2,4,6-Tri-(di-isobutylamino)-1,3,5-triazine	—	(Fp. 91°C)	—	—	—
XI	2,4,6-Tri-(N-butylanilino)-1,3,5-triazine	—	(Fp. 70°C)	—	—	—
	2. Group					
XII	2,4-Di-(di-ethylamino)-6-di-n-butylamino-1,3,5-triazine	167…172	— 44	79,6	7,3	32
XIII	2,4-Di-(di-n-butylamino)-6-di-äthylamino-1,3,5-triazine	195…200	— 49	100,9	9,9	82
XIV	2,4-Di-(di-n-propylamino)-6-di-n-butylamino-1,3,5-triazine	188…194	(Fp. -31°C)	128,6	10,8	66
XV	2,4-Di-(di-n-butylamino)-6-di-n-propylamino-1,3,5-triazine	200…205	— 50	126,9	11,6	84
XVI	2,4-Di-(di-n-butylamino)-6-di-n-hexylamino-1,3,5-triazine	241…245	— 50	119,8	12,8	107
XVII	2,4-Di-(di-n-hexylamino)-6-di-n-butylamino-1,3,5-triazine	267…269	— 55	112,6	12,7	113
XVIII	2,4-Di-(di-n-propylamino)-6-di-n-hexylamino-1,3,5-triazine	217…224	— 51	113,8	10,8	85
XIX	2,4-Di-(di-n-hexylamino)-6-di-n-propylamino-1,3,5-triazine	248…253	— 52	104,8	11,3	103
XX	2,4-Di-(di-ethylamino)-6-di-n-hexylamino-1,3,5-triazine	205…209	— 50	78,7	8,1	73
XXI	2,4-Di-(di-n-hexylamino)-6-di-äthylamino-1,3,5-triazine	251…257	— 55	95,4	11,1	109
XXII	2,4-Di-(di-n-butylamino)-6-di-n-octylamino-1,3,5-triazine	267…273	— 52	108,0	12,6	115
XXIII	2,4-Di-(di-n-hexylamino)-6-di-n-octylamino-1,3,5-triazine	290…292	(Fp. —7°C)	106,5	13,4	123
XXIV	2,4-Di-(di-n-butylamino)-6-di-isopropylamino-1,3,5-triazine	194…196	— 25	338,7	17,9	48
XXV	2,4-Di-(di-n-hexylamino)-6-di-isopropylamino-1,3,5-triazine	248…255	— 39	203,4	15,9	87
XXVI	2,4-Di-(di-n-butylamino)-6-di-isobutylamino-1,3,5-triazine	205…207	— 28	355,9	18,8	52
XXVII	2,4-Di-(di-isobutylamino)-6-di-n-butylamino-1,3,5-triazine	190…194	— 5	1 304,7	24,9	—100
XXVIII	2,4-Di-(di-n-butylamino)-6-di-(2-äthylhexyl)-amino-1,3,5-triazine	238…241	— 31	471,1	23,3	62
XXIX	2,4-Di-(di-(2-äthylhexyl)-amino-6-di-n-butylamino-1,3,5-triazine	257…263	— 23	568,9	26,9	68
XXX	2,4-Di-(di-n-butylamino)-6-N-butylanilino-1,3,5-triazine	234…238	— 31	250,1	18,5	89
XXXI	2,4-Di-(N-butylanilino)-6-di-n-butylamino-1,3,5-triazine	249…253	— 17	613,7	27,8	66
XXXII	2,4-Di-(di-n-butylamino)-6-N-äthyl-p-toluidino-1,3,5-triazine	230…233	— 34	251,5	16,7	70
XXXIII	2,4-Di(di-n-butylamino)-6-N-benzyl-isopropylamino-1,3,5-triazine	233…235	— 23	410,2	20,8	56
XXXIV	2,4-Di(di-n-butylamino)-6-N-äthyl-cyclohexylamino-1,3,5-triazine	231…233	— 20	663,0	26,8	61
	3. Group					
XXXV	2-Di-ethylamino-4-di-n-butylamino-6-di-n-hexylamino-1,3,5-triazine	255…263**)	— 56	93,4	10,3	100
XXXVI	2-Di-ethylamino-4-di-n-propylamino-6-di-n-butylamino-1,3,5-triazine	193…197	— 46	99,7	8,9	59
XXXVII	2-Di-n-butylamino-4-di-n-hexylamino-6-di-n-octylamino-1,3,5-triazine	285…287	— 60	102,8	12,7	120
XXXVIII	2-Di-ethylamino-4-di-n-butylamino-6-N-butylanilino-1,3,5-triazine	220…225	— 33	216,6	14,7	64
XXXIX	2-Di-n-butylamino-4-di-n-hexylamino-6-N-butylanilino-1,3,5-triazine	270…277	— 36	265,4	19,5	91

*An isomer mixture of dipentyl amines was used in the synthesis

**Boiling points of Group 3 were measured at 5 mm Hg.

The prepared compounds can be classified into the following three groups:

1. Compounds in which the R substituents of the three amino groups are identical.

2. Compounds in which two amino groups contain the same substituents.

3. Compounds in which the three amino groups contain always different R substituents.

The compounds of Group I with the exception of compound XI correspond to the general formula (I), while Groups 2 and 3 contain compounds represented by the general formula (I) as well as by formula (II).

Correlations between physical properties and chemical composition

Boiling point

The boiling point increases almost linearly with increasing molecular weight for the 2,4,6-tri-(di-n-alkylamino)-1,3,5-triazines (Table 1. IV, XII, XX, XIV, XIII, XV, VI, XVIII, XXI, XVI, XIX, XVII, XXII, VIII, XXIII, IX) (Fig. 2). The boiling point of symmetrically and asymmetrically substituted compounds of equal molecular weight (Table 1, for example VI, XVIII) is only slightly different. On introduction of iso-alkyl groups the boiling point decreases as expected (Table 1. I, VI, XXVI, XXVII, XV, XXIV).

Pour point (DIN 51597)

From the symmetrically substituted alkyl melamines (Group I, Table 1) only compounds VI, and VII are liquids at room temperature. Compound VII represents an exception, because we are dealing with a mixture of isomers rather than a pure compound, since technical sec-pentylamine was used in the synthesis. The other compounds, which are solids at room temperature, showed

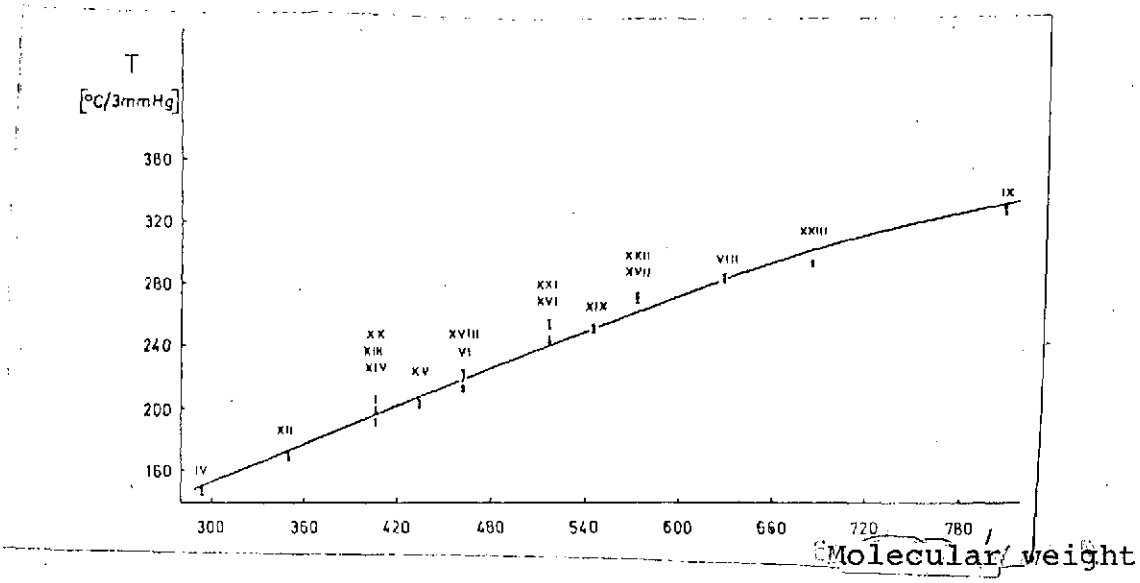

Fig. 2. Boiling point of symmetrical and asymmetrical n-alkylated melamines as a function of molecular weight.

a melting point in the 12 to 165°C temperature range. These relatively high melting points can be attributed to the symmetrical structure of the molecule.

Liquids with low freezing point can be obtained only when the structure of the n-alkyl melamines is asymmetrical. The results also indicate that the pour point decreases with increasing molecular asymmetry; thus the tri-(di-alkyl)-malamines, in which only two amino groups are identically alkylated (Group 2, XII - XXIII, Table 1) have pour point values in the -7 to -55°C range, a great majority of the compounds investigated has a pour point below -50°C.

A further increase of molecular asymmetry, by different /319
alkylation of all three amino groups, results in pour point values up to -60°C (Table 1, XXXVII). An introduction of iso-alkyl groups (Table 1, XXIV-XXIX), aryl- and alkylated aryl-

groups (Table 1, XXX-XXXIII, XXXVIII, XXXIX), and also cycloalkyl-groups (Table 1, XXXIV) resulted in all cases investigated in a well pronounced increase in the pour point.

Viscosity

The viscosity data of 2,4,6-tri-(di-alkylamino)-1,3,5-triazines containing straight side chains (Table 1, IV, VI-VIII, XII-XXIII, XXXV-XXXVII) were at 100°F in the 64.4 to 128.6 cSt range, and at 210°F in the 5.4 to 13.4 cSt range. It was not possible to establish an unequivocal relationship between the viscosity and chain length of the alkyl group for symmetrical alkylated melamines.

On introduction of iso-alkyl groups (Table 1, XXIV-XXVIII) the viscosity increases as expected. The viscosity values are in the 203.5 to 1304.7 cSt range at 100°F and in the 15.9 to 24.9 cSt range at 210°F. This increase is well pronounced in case of compounds VI, XXVI, XXVII. On successive exchange of two n-butyl groups with two iso-butyl groups the viscosity increases in this series at 100°F from 127.9 to 1304.7 cSt, and at 210°F from 12.6 to 24.9 cSt.

A similar increase in viscosity results from the introduction of aryl-groups (XXX, XXXI, XXXVIII, XXXIX), alkylated aryl-groups (XXXII), and cycloalkyl groups (XXXIV).

The viscosity of asymmetrically alkylated melamines (ν_{total}) with straight side chains can be estimated from the viscosity ($\nu_{1...n}$) of the corresponding derivatives using the following basic considerations. It was assumed that the total viscosity of symmetrically alkylated melamines (ν_{total}) is an additive property of the values ν_R and $y(\nu_{a_{1...n}})$, which correspond to the structural elements of formula XL (Fig. 1).

The viscosity can be calculated by the formula

$$\nu_{1\ldots n} = \nu_k + 3(\nu_{a\,1\ldots n}) \qquad (1)$$

The viscosity of a compound with different side chains (XLI) can be estimated from the viscosity of the corresponding symmetrical alkyl melamines (Fig. 1). In this case, equation (1) must be expanded according to $\nu_{a\,1\ldots n}$ and gives equation (2)

$$\nu_{Total} = \nu_k + \nu_{a_1} + \nu_{a_2} + \nu_{a_3}$$

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from which

$$\nu_{Total} = \frac{\nu_1 + \nu_2 + \nu_3}{3}$$

Table 2 shows for the individual asymmetrical alkylated melamines the values calculated by this method and compares them with the measured viscosities at 100°F and 210°F. The maximum deviation between corresponding values is 9.5%.

Table 2

Measured and calculated viscosity of asymmetrical alkylated melamines

Number	Compound	Viscosity (cSt) 100°F measured	100°F calculated	210°F measured	210°F calculated
XII	2,4-Di-(di-äthylamino)-6-di-n-butylamino-1,3,5-triazine	79,6	85,6	7,3	7,8
XIII	2,4-Di-(di-n-butylamino)-6-di-äthylamino-1,3,5-triazine	100,9	106,7	9,9	10,2
XVI	2,4-Di-(di-n-butylamino)-6-di-n-hexylamino-1,3,5-triazine	119,8	123,3	12,8	12,9
XX	2,4-Di(di-äthylamino)-6-di-n-hexylamino-1,3,5-triazine	78,7	81,0	8,1	8,1
XXI	2,4-Di-(di-n-hexylamino)-6-di-äthylamino-1,3,5-triazine	95,4	97,5	11,1	10,7
XXXV	2-Di-äthylamino-4-di-n-butylamino-6-di-n-hexylamino-1,3,5-triazine	93,4	102,1	10,3	10,5
XXII	2,4-Di-(di-n-butylamino)-6-di-n-octylamino-1,3,5-triazine	108,0		12,6	13,0
XXIII	2,4-Di-(di-n-hexylamino)-6-di-n-octylamino-1,3,5-triazine	106,5		13,1	13,5
XIV	2,4-Di-(di-n-propylamino)-6-di-n-butylamino-1,3,5-triazine	128,6		10,8	11,0
XV	2,4-Di(di-n-butylamino)-6-di-n-propylamino-1,3,5-triazine	126,9		11,6	11,8
XVIII	2,4-Di-(di-n-propylamino)-6-di-n-hexylamino-1,3,5-triazine	113,8		10,8	11,3
XIX	2,4-Di-(di-n-hexylamino)-6-di-n-propylamino-1,3,5-triazine	104,8		11,3	12,4
XXXVI	2-Di-äthylamino-4-di-n-propylamino-6-di-n-butylamino-1,3,5-triazine	99,7		8,9	9,4

For compounds XXII, XXIII, XIV, XV, XVIII, XIX, and XXXVI the viscosity could not be calculated at 100°F since the corresponding symmetrical alkyl melamines are solids at this temperature.

Viscosity - temperature relationship

The viscosity-temperature relationship of the symmetrical compounds was characterized by the determination of the viscosity index (V.I.) according to DIN 51563. For symmetrical alkylated melamines (Table 1, IV-VIII) a pronounced increase of the V.I. was observed with increasing chain length of the alkyl group. A V.I. increase from 81 to 118 resulted from a chain length increase from C_2 to C_6. The V.I. values ranged from 32 to 123 for asymmetrically alkylated melamines.

According to the determined data, the viscosity-temperature dependence is primarily determined by the number of CH_2- and CH_3- groups present in the form of n-alkyl substituents and not so much by the symmetry or asymmetry of the entire molecule. As an example, compounds XIV and XX (Table 1) can be mentioned. The total number of C-atoms present in the alkyl groups is in each case 20, and was obtained in one case by combination of n-butyl and n-propyl groups, in the other compound by combination of ethyl and n-hexyl groups. Although the structure of these compounds is significantly different, the V.I. values of 66 and 73 are in the same range.

The relationships can be further clarified by Fig. 3, which shows that the V.I. values of n-alkylated melamines increase steadily with increasing molecular weight or with an increasing number of C-atoms (ΣC_{alkyl}) present in the alkyl groups. An introduction of other substituents at the amino groups (iso-alkyl, aryl-, or alkylated aryl-, or cycloalkyl-

groups) resulted in all cases investigated in a deterioration of the viscosity-temperature relationship. In Fig. 3 the V.I. values of all these compounds are located clearly below the curve determined by the n-alkylated melamines.

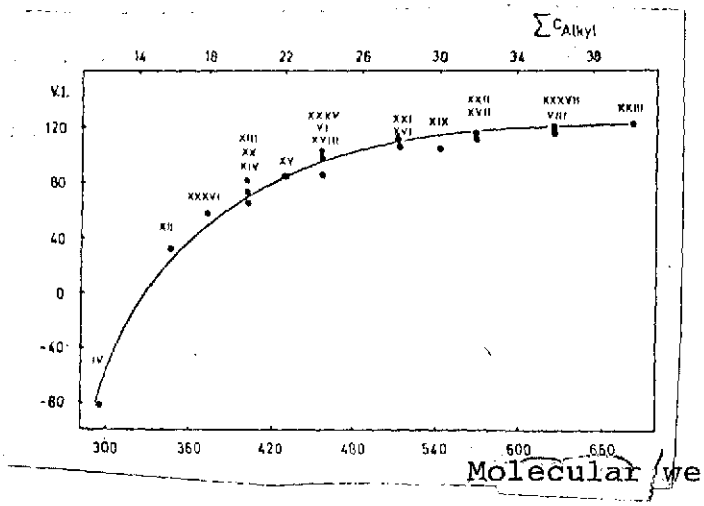

Figure 3. V.I. of n-alkylated melamines as a function of molecular weight or ΣC_{alkyl}.

Oxidation stability and thermal stability

Lubricating oils are frequently exposed in the practice to elevated temperatures and during this exposure they can be in contact with the oxygen of the air and also with oxidation catalysts such as metals and metal compounds.

The resulting changes are called "aging". The products of aging are on one hand acids formed in oxidation processes, and on the other hand high molecular weight produced by oxidation and polymerization reactions. Furthermore, an exclusively thermal stress of the oil, without access of oxygen, can also lead to aging. For this reason, lubricants are usually tested in two directions. In one case the lubricants are tested at elevated temperature in the presence of oxygen, in the other case under exclusion of oxygen.

The following investigation of the oxidation and thermal stability was made using the apparatus developed by Spengler and Jantzen [7] for the aging of aviation oils. /321

Oxidation stability

To determine the thermo-oxidation stability, a series of selected 2,4,6-tri-(di-alkylamino)-1,3,5-triazines was aged for 24 hours by passing 10 liters per hour of air at temperatures from 120 to 210°C. To determine the oxidation stability, the change of viscosity, neutralization number, and pour point were measured as a function of aging temperature. As an example, the results for 5 alkyl melamines are given in Table 3, and as a comparison, the determined viscosity changes for n-heptoic acid pentaerythrit ester and a polyphenyl ether (for example 5P4A) for identical aging conditions are included.

For all alkyl melamines investigated a noticeable increase was observed in the 125 to 130°C aging temperature range caused by oxidation reactions. At aging temperatures in the 195 to 210°C range the viscosity increase was generally 300% of the viscosity of the fresh oil at 100°F.

It was shown on the example of compounds XIII, XVI, and XVII (Table 3) that the pour point of the modified compounds increases with increasing aging temperature.

Table 3

Changes of viscosity, pour point, and neutralization number resulting from oxidative aging of 2, 4, 6-tri(-di-alkylamino)-1, 3, 5-trizines
(Aging conditions: 24 hrs., 10l/hr air)

Number	Compound	Aging temp. °C	Viscosity increase (400°F) %	Pour point °C	Neutralization number mg KOH/g oil
VI	2,4,6-Tri-(di-n-butylamino)-1,3,5-triazine				*) 0,074
		130,2	0,36		—
		142,2	4,7		—
		159,9	61,3		1,16
		162,5	73,53		
		181,9	114,54		0,45
		198,0	188,46		1,74
		210,9	369,22		1,83
XIII	2,4-Di-(di-n-butylamino)-6-di-ethylamino-1,3,5-triazine			*) 49	*) 0,021
		120,2	1,26		
		142,1	21,92	45	
		162,4	79,35	37	1,06
		182,0	119,35	26	0,80
		197,9	211,18	17	1,73
		210,8	303,12	10	1,68
XVI	2,4-Di-(di-n-butylamino)-6-di-n-hexylamino-1,3,5-triazine			*) 50	*) 0,013
		120,2	0,72		—
		142,0	1,27	46	
		159,7	60,1	38	1,72
		162,3	69,03		—
		181,9	117,16	28	1,06
		197,9	204,0	21	1,64
		210,7	342,79	13	1,78
XVII	2,4-Di-(di-n-hexylamino)-6-di-n-butylamino-1,3,5-triazine			*) 55	
		142,1	1,54	50	
		148,0	9,11	—	
		162,2	29,46		
		162,4	65,08	35	
		182,0	109,0	24	—
		197,9	164,52	12	—
XXII	2,4-Di-(di-n-butylamino)-6-di-n-octylamino-1,3,5-triazine				*) 0,021
		148,0	17,36	—	—
		162,3	62,69		2,41
		182,1	108,64		1,18
		197,9	190,59		3,34
		210,9	423,77		1,01
	n-heptoic acid pentaerythrit-ester	140	59,6	—	—
		160	243,8	—	—
		180	555,47	—	—
		200	1 071,8	—	—
	Polyphenylether (5 P 4 Å)	220	3,8	—	—
		300	11,1	—	—
		316	17,0	—	—
		330	39,2	—	—
		345	190,0	—	—

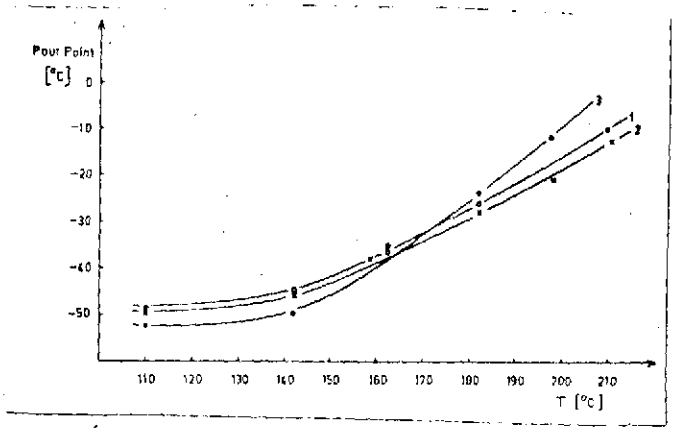

Figure 4. Pour point as a function of aging temperature
1) 2,4-di-(di-n-butylamino)-6-di-ethylamino-1,3,5-triazine
2) 2,4-di-(di-n-butylamino)-6-di-n-hexylamino-1,3,5-triazine
3) 2,4-di-(di-n-hexylamino)-6-di-n-butylamino-1,3,5-triazine

The determination of the neutralization number of the oxidatively aged alkyl melamines did not show a steep increase in the neutralization number with increasing aging temperature. This result can be explained by two causes: first, the organic acids formed in the oxidation process are highly volatile, and second, the carbonic acids formed in the oxidation can react with the tertiary amino groups of the alkyl melamines forming salts and then they cannot be determined unequivocally by potentiometric titration.

By comparing the oxidation stability on the basis of the viscosity change and aging temperature relationship for the alkyl melamines with that for the n-heptoic acid pentaerythrit ester and polyphenyl ether (for example 5P4A) (Fig. 5), it can be seen that the oxidation stability is somewhat lower than that of the exceptionally stable polyphenyl ether, but significantly better than that of the sterically hindered esters.

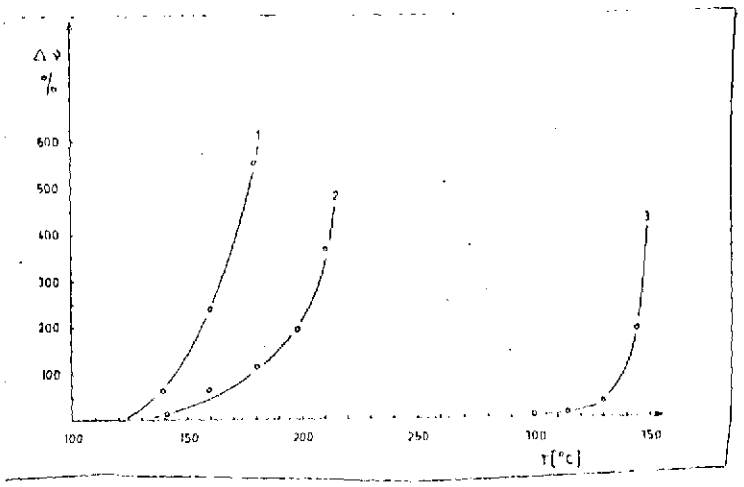

Figure 5. The viscosity increase in percent at 100°F as a function of temperature

1) n-heptoic acid pentaerythrit ester
2) 2,4,6-tri-(di-n-butylamino)-1,3,5-triazine
3) Polyphenyl ether (for example 5P4A)

Thermal stability

To investigate the thermal stability, compounds VI, XIII, XVI, XXII, XXV, and XXX were aged for 24 hours in the 320 to 370°C temperature range in a nitrogen atmosphere.

The thermal change of the synthetic fluids was determined by measurement of the viscosity change after aging. The percent viscosity change was evaluated as a function of aging temperature (Table 4).

In the investigation of alkyl melamines in the temperature range up to 330°C only a slight viscosity increase, about 1%, was observed. A steep increase in the viscosity, which indicates a significant thermal change of the synthetic oils, occurs

only in the 350 to 360°C temperature range.

Table 4

Increase of viscosity after thermal aging of 2,4,6-tri-(di-alkylamino)-1,3,5 triazines. Aging conditions: 24 hours, nitrogen atmosphere.

Number	Compound	Aging temp. °C	Viscosity increase (100°F) %
VI	2,4,6-Tri-(di-n-butylamino)-1,3,5-triazine	325,3	6,68
		344,3	8,69
		358,9	10,67
		370,0	194,25
XIII	2,4-Di-(di-n-butylamino)-6-diethylamino-1,3,5-triazine	325,3	0,4
		346,0	10,31
		358,9	37,43
		370,0	80,15
XVI	2,4-Di-(di-n-butylamino)-6-di-n-hexylamino-1,3,5-triazine	326,0	1,06
		346,0	63,11
		360,1	56,39
		365,7	158,31
XXII	2,4-Di-(di-n-butylamino)-6-di-n-octylamino-1,3,5-triazine	326,0	0,61
		346,0	3,31
		354,8	26,79
		365,7	199,62
XXV	2,4-Di-(di-n-hexylamino)-6-di-isopropylamino-1,3,5-triazine	325,3	0,49
		344,3	14,89
		358,9	30,67
		364,2	142,12
XXX	2,4-Di-(di-n-butylamino)-6-N-butylanilino-1,3,5-triazine	326,0	0,98
		344,3	17,72
		354,8	74,77
		360,1	109,59
	n-Valeriansäure-pentaerythrit-ester*)	280	2,2
		300	6,3
		320	20,7
		350	130,3

* The sterically hindered ester was investigated in the same way for comparison.

Figure 6 shows on the example of 2,4,6-tri-(di-n-butyl-amino)-1,3,5-triazine a comparison of the thermal stability based on the viscosity change for an alkyl melamine and a sterically hindered ester. /322

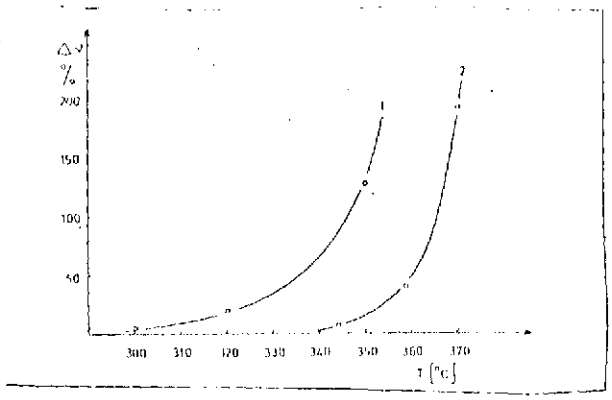

Figure 6. Percent viscosity change at different aging temperatures. I) n-valeric acid pentaerythrit ester, II) 2,4,6-tri-(di-n-butylamino)-1,3,5-triazine

The thermal stability of the alkyl melamine is clearly higher than that of the pentaerythrit ester. As it is known from the literature, polyphenyl ether (for example 5P4A), used exclusively as a lubricant for high speed aircraft, shows at 465°C a steep increase of viscosity [8]. The thermal stability of the alkyl melamines indicates, that the thermal decomposition, as it is also assumed in the case of sterically hindered esters [9], follows the path of radical reactions through energetically favored transition states, as it occurs in the case of dicarbonic acid esters. This assumption was confirmed by the results of the IR-spectral investigation of thermally changed compounds which did not give indications of the rearrangements of alkyl melamines into alkyl iso-melamines. This is in agreement with the results obtained by Thurston [10], according to which in the case of the alkyl melamines the melamine form is more stable then the iso-melamine form, although this is not the case for the 2,4,6--ri-alkoxy-1,3,5-triazines [6].

A detailed investigation of the chemical path of the thermal and oxidative decomposition of the 2,4,6-tri-(dialkylamino)-1,3,5-triazines should be carried out as a continuation of the work reported here.

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